CANADA

DEPARTMENT OF ENERGY, MINES AND RESOURCES

MINES BRANCH

OTTAWA

PHYSICAL METALLURGY DIVISION

INTERNAL REPORT PM-R-74-10

INVESTIGATION OF A PRACTICAL METHOD FOR MEASURING THE SURFACE AREA OF METAL POWDERS

by

C. F. Dixon

Nuclear and Powder Metallurgy Section

July 31, 1974

90-04660/

PHYSICAL METALLURGY DIVISION

INTERNAL REPORT PM-R-74-10

INVESTIGATION OF A PRACTICAL METHOD FOR MEASURING THE SURFACE AREA OF METAL POWDERS

by

C. F. Dixon*

ABSTRACT

Electroless nickel plating of iron powders was investigated as a possible simpler and cheaper means of determining total surface area. Areas of the powders were calculated from the weight and thickness of the nickel film deposited, but values were found to be lower than measurements made by the BET gas adsorption technique. This is believed to be due to the impossibility of obtaining a sufficiently thin nickel deposit.

---

*Physical Scientist, Nuclear and Powder Metallurgy Section, Physical Metallurgy Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

INTRODUCTION

The surface area of metal powders is an important parameter in characterizing physical and metallurgical properties such as sinterability, compressibility, interparticle frictional forces, and green strength. The method normally used to determine surface area of metal powders is the BET (Brunauer, Emmett, and Teller) gas adsorption method[1,2]. This method relies on the principle that, under certain circumstances, gas may become absorbed on the surface of powder particles to form monomolecular layers and the amount of gas absorbed for a known weight of powder is determined. Disadvantages that restrict the use of the BET method are the high cost of the necessary apparatus and the length of time required for analyses. The object of this investigation was to examine the feasibility of developing a simple and economical method of measuring surface area. The concept investigated was that of depositing a thin, uniform coating of a known thickness of a suitable metal on all powder particles and calculating the area from the weight gain. For many metal powders, and particularly iron powders, a convenient coating process and material is electroless nickel plating. In this investigation, two iron powders were plated using a commercial, electroless nickel-plating solution.

The area of the powders were calculated according to the equation:

$$\text{Area of Powder} = \frac{\text{Weight of Ni plated on the powder} \times \text{Area of a control specimen}}{\text{Weight of Ni plated on control specimen}}$$

The powder and the control specimen, of known area, were plated at the same time so that the rate of plating would be the same on both. This equation is valid for flat surfaces and will apply to curved surfaces if the nickel film is thin compared to the radius of the curved surface, as is explained in Appendix A.

Because metal powders can seldom be considered to have flat surfaces, it was necessary to determine the plating conditions that would permit the deposit of a continuous film of nickel of minimum thickness. The thickness of the nickel film was determined by dividing the weight gain of the control specimen, after plating, by the area of the specimen and by the density of the nickel, plated from the solution(7.9 g/cc, supplied by the manufacturer).

PROCEDURE

Materials

The two iron powders used were 300-M, an atomized powder produced by A.O. Smith Corp., and MET-1, an iron carbonyl powder produced by General Aniline and Film Corp. The sieve analyses of these powders, shown in Table 1, were taken from another report[3]. The electroless nickel-plating solution used was "Wingate 700" produced by Patchlin Chemical Co.

TABLE 1

Sieve Analysis

Iron Powder	Sieve Analysis, wt% (U.S. Sieve Nos.)						
	+177 µm (+80)	-177+149 µm (-80+100)	-149+105 µm (-100+140)	-105+74 µm (-140+200)	-74+63 µm (-200+230)	-63+44 µm (-230+325)	-44 µm (-325)
300-M	trace	0.6	16.7	16.3	13.7	20.5	32.2
MET-1	42.8	10.1	18.4	7.3	3.9	4.7	12.8

Plating

The recommended plating conditions for the Winplate 700 solution are: 88 to 93°C (190 to 200°F), a pH of 5.5 to 6.0, and a nickel concentration in the bath of 4.4 to 11.2 g/ℓ.

In this investigation, one gram sample of the iron powders and a control specimen of Armco iron (21.8 cm^2) were dried at 100°C (212°F) for 1 hr, cooled, weighed on an analytical balance accurate to 10^{-4} g, then plated at the temperatures, times, and levels of pH listed in Table 2. After plating, the powder was filtered from the solution in a Gooch crucible. The powder and the control specimen were then washed with distilled water and dried at 100°C (212°F) for 1 hr, cooled and weighed. The nickel concentration in the plating bath was 8 g/ℓ for the 300-M powder and 16 g/ℓ for the MET-1 powder. The volume of the plating bath was 400 mℓ. During plating, the bath was stirred by a flow of argon, as indicated in a diagramatic sketch of the apparatus in Figure 1.

TABLE 2

Plating Results

Powder	Plating Temp, °C	Plating Time (min)	pH	Powder Wt Gain/g	Sample Wt Gain (g)	Surface Area m^2/g		Thickness of Ni Plate μm
300-M	76	5	5.39	0.031	0.006	-		0.35
300-M	76	5	5.75	0.027	0.004	-		0.23
300-M	76	5	6.10	0.040	0	-		-
300-M	82	5	5.52	0.037	0	-		-
300-M	82	5	5.72	0.072	0.004	-		0.23
300-M	82	5	6.02	0.063	0.001	-		0.06
300-M	86	2	6.01	0.046	0.003	0.033		0.20
300-M	86	5	5.55	0.079	0.007	0.025		0.40
300-M	86	5	5.81	0.077	0.007	0.024	Av	0.40
300-M	86	5	6.07	0.079	0.007	0.025	0.025	0.40
300-M	90	2	5.99	0.070	0.005	0.030		0.30
300-M	90	5	5.50	0.126	0.010	0.027		0.58
300-M	90	5	5.78	0.107	0.010	0.023	Av	0.58
300-M	90	5	6.10	0.109	0.010	0.024	0.025	0.58
300-M	90	15	5.87	0.254	0.035	0.016		2.03
MET-1	90	5	6.00	0.175	0.007	0.054	Av	0.40
MET-1	90	5	5.90	0.164	0.008	0.045	0.051	0.45
MET-1	90	5	5.92	0.169	0.007	0.053		0.40
300-M	-	-	-	-	-	0.049*		-
MET-1	-	-	-	-	-	0.247*		-

* BET Measurements taken from another report (3)

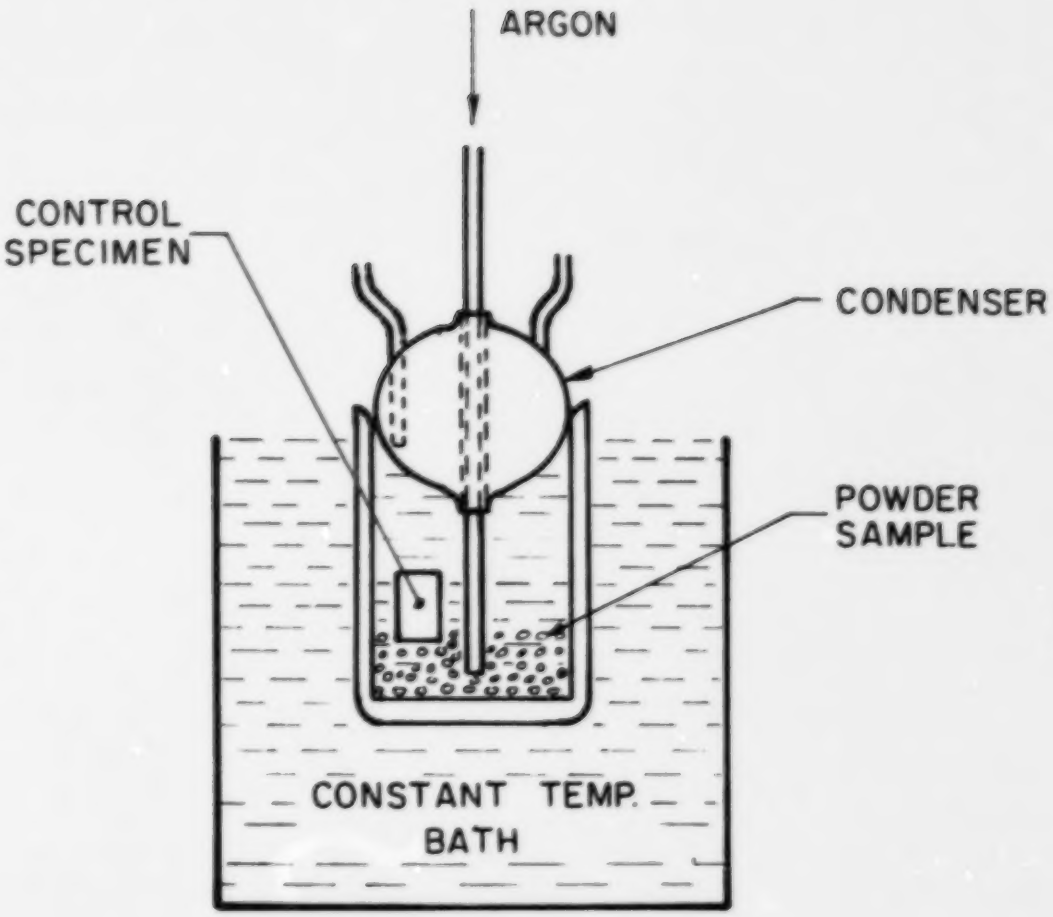


Figure 1. Plating Apparatus.

The same control specimen was used during the plating of all powder samples; so was, in fact, a nickel-plated specimen.

RESULTS AND DISCUSSION

Effect of Bath Temperature

The plating results listed in Table 2 show that the weight gains for the 300-M powder were erratic when the plating was carried out at 76 and 82°C (167 and 180°F) for 5 min, but consistent when the plating was done at 86 and 90°C (187 and 194°F). Because the thickness of the nickel film was greater at 90°C (194°F) and the object was to have a continuous thin film, higher plating temperatures were not considered. This restricted the plating temperature to the 86 to 90°C (187 to 194°F) range. The nickel film plated on the powders at these temperatures was continuous as can be seen by examining the electron scanning photomicrograph of the 300-M powder, plated at 86°C (187°F) for 5 min, shown in Figure 2. This can be compared to the powder particle surface before plating shown in Figure 3.

Effect of Nickel Concentration in Bath

Nickel concentrations in the bath were kept within the recommended levels for the 300-M powder; but, when the MET-1 powder was plated, it was necessary to double the concentration to obtain reproducible weight gains. A comparison of the surface areas of the two powders as determined by the BET method (0.049 m^2/g for 300-M and 0.247 m^2/g for MET-1), included in Table 2,

3250X

Figure 2. Nickel-Plated 300-M Powder.

3250X

Figure 3. 300-M Powder.

shows that the MET-1 powder has a much larger surface area. This suggested that, to obtain consistent plating results, a minimum concentration of nickel was necessary in the 400 mℓ bath for a given surface area. For this reason, no attempt was made to reduce the thickness of the nickel film by reducing the nickel concentration of the bath.

Effect of pH of Bath

No effect of pH on the rate of plating was observed for the pH levels used.

Effect of Plating Time

The surface area determined for the 300-M powder by plating at 86°C (187°F) for 5 min, 0.024 m^2/g, was half that obtained by the BET method. The thickness of the nickel film was 0.4 μm. Decreasing the plating time to 2 min reduced the thickness of the film to 0.2 μm and increased the calculated surface area to 0.033 m^2/g. Shorter plating times were not considered practical. Increasing the plating time to 15 min, of course, had the opposite effect (Table 2).

Influence of Film Thickness on Surface Area Determinations

The results show that the thinner the nickel film the closer the calculated surface area to the BET value. However, to obtain values comparable to those obtained by the BET method a thinner film than was obtained in this investigation, 0.2 μm, will be required. From the plot of calculated surface area versus thickness of nickel film in Figure 4, it would appear that the film thickness should be in the vicinity of 0.02 μm, or less.

Consideration of this problem in Appendix A suggests that the thickness of the nickel film plated on the powder particles was large in comparison to the radius of curvature of the surface of the particles. The sieve analyses in Table 1 show that 68.8% of the 300-M powder particles and 87.2% of the MET-1 powder particles were larger than 44 μm; so the radius of these particles, if they were spheres, would be 22 μm or greater. This compared to 0.2 μm for the thickness of the nickel film should give the magnitude of difference necessary for accurate surface area measurements, particularly in the case of the MET-1 powder which had 42.8% of the particles larger than 177 μm. Because the results show that a nickel film thinner than 0.2 μm is required, it is evident that the size of the powder particles is not the main factor dictating the thickness of the nickel film. Examination of the powders by the electron scan microscope showed the surface of some of the powder particles to consist of many small partially formed spheres as is shown in Figures 5 and 6 (300-M and MET-1 powders, respectively). The film thickness would then have to be small compared to the radius of these spheres rather than to the radius of the powder particles.

When the film is too thick, as in this investigation, the surface area determinations will be low and the error will not be the same for each powder. This is shown in the results in Table 2. The calculated surface areas for MET-1 and 300-M powders, when plated with approximately the same thickness of nickel (0.40 μm), were 1/3 and 1/2, respectively, that of the areas calculated by the BET method.

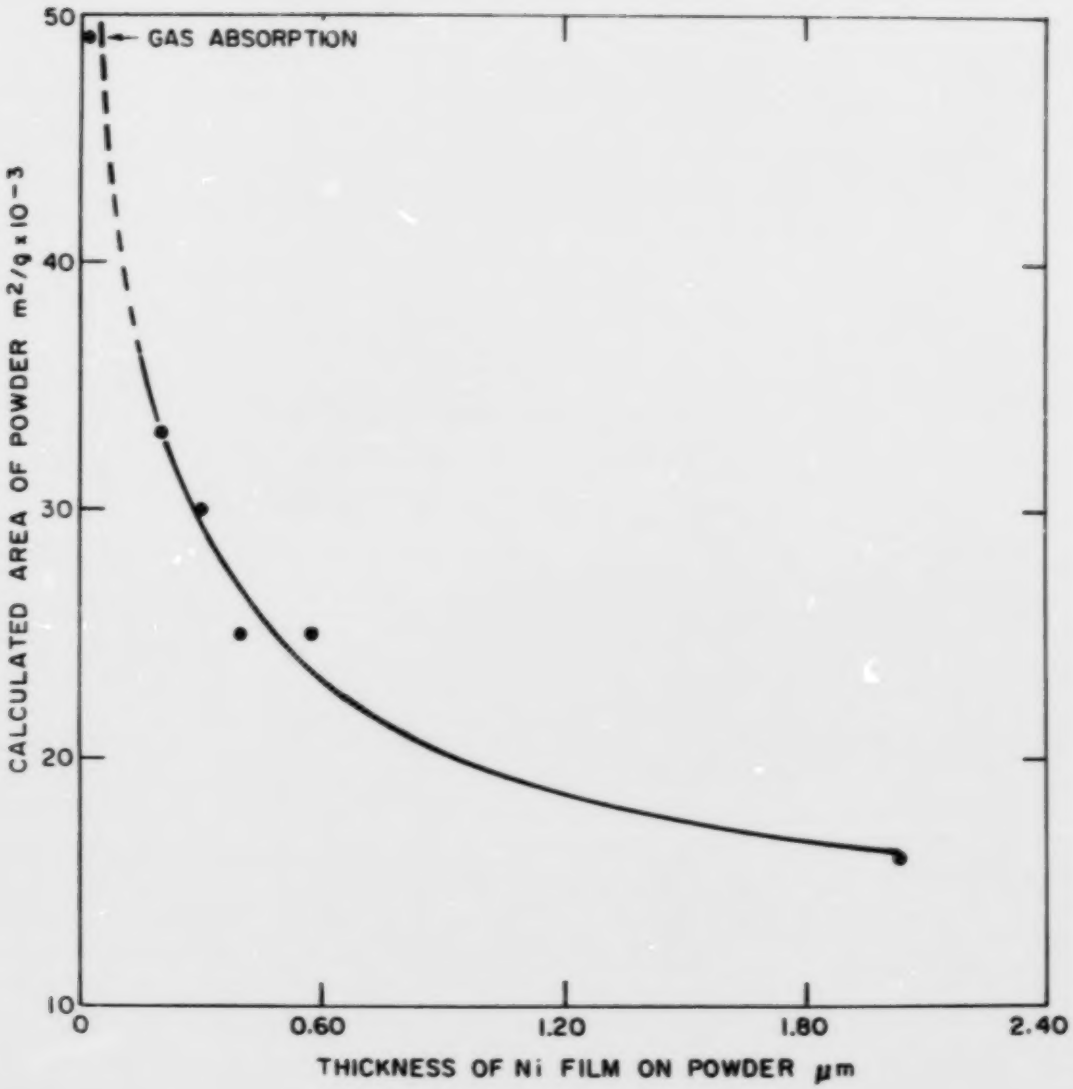
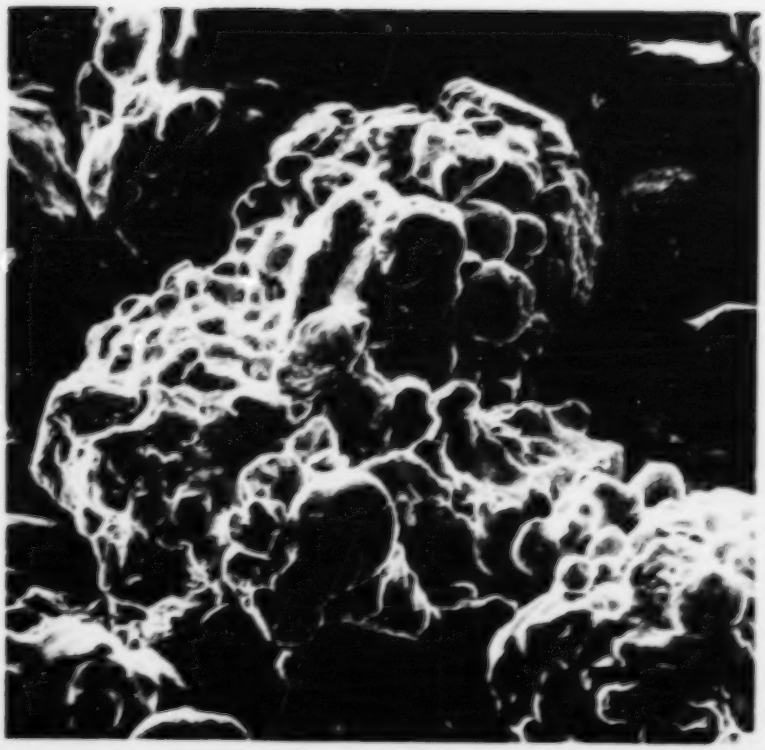
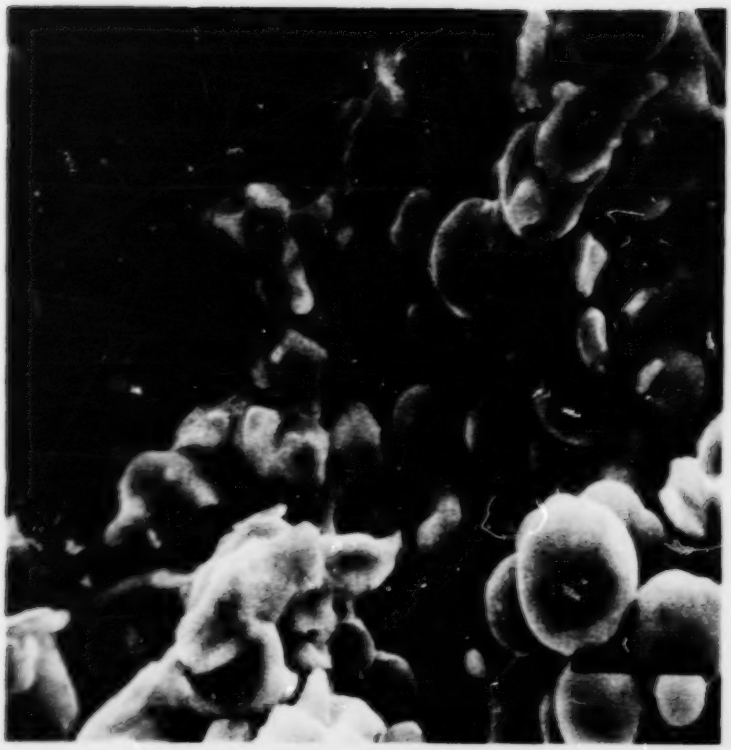


Figure 4. Thickness of Ni Film on Powders vs Calculated Area of Powders.



600X

Figure 5. 300-M Powder



3200X

Figure 6. MET-1 Powder

Powder Dissolved in Bath

Chemical analyses of the baths after plating showed that in the order of 0.004 g of iron powder dissolved during plating. This was included in calculating the surface areas, but had a minimal effect on the results.

CONCLUSIONS

Nickel films, from 0.20 to 2.03 μm thick, were plated on iron powder particles using an electroless nickel plating solution. Surface areas calculated from the weight and thickness of nickel films gave low results because the films were too thick. From the results obtained, it is estimated that a film thickness of 0.02 μm or less would be necessary in order to obtain values for the surface areas comparable to those obtained by the BET method

ACKNOWLEDGEMENTS

The author wishes to thank Dr. K. M. Pickwick, Metal Physics Section, Physical Metallurgy Division, for preparing the electron scanning photomicrographs and Dr. S. M. Ahmed, Physical Chemistry Section, Mineral Sciences Division for the BET surface area measurements.

REFERENCES

1. S. Brunauer, P. Emmeth, and E. Teller; Adsorption of Gases in Multimolecular Layers; J. Amer. Chem. Soc., vol. 60, pp 309 to 319, February 1938.

2. B. Lippens and M. Hermans; Measurement of the Surface Area of Powders by the BET Method; Powder Metallurgy, No. 7, pp 66 to 81, 1961.

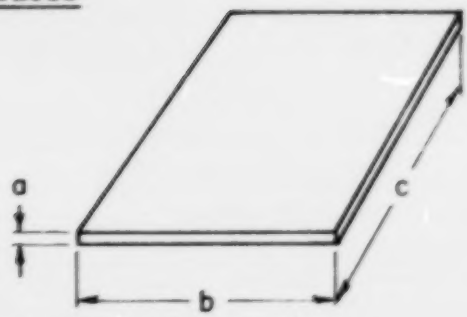
3. H. M. Skelly; Properties and Compacting Behaviour of Various Iron Powders, Mines Branch Internal Report PM-R-73-4, January 1973.

ea

APPENDIX

Nickel Plating

For Flat Surfaces



Area of flat sheet = $2(ab+ac+bc)$

Volume of nickel plated on sheet = Area of sheet (A) x thickness of Ni plate (t)

Also, volume of nickel plated on sheet = $\frac{\text{Weight of Ni plated } (\omega)}{\text{density of Ni plated } (\rho)}$

Therefore $A \times t = \frac{\omega}{\rho}$

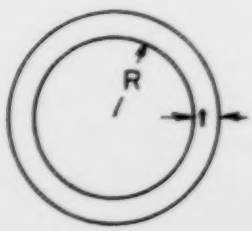
or $A = \frac{\omega}{\rho t}$

For metal powders (with flat surfaces) plated at the same time as a flat control specimen, the thickness of the nickel plated will be the same on both

Therefore $\frac{\text{Area of powder}}{\text{Area of control specimen}} = \frac{\frac{\text{wt of Ni on powder}}{\rho t}}{\frac{\text{wt of Ni on control specimen}}{\rho t}}$

or $\text{Area of powder} = \frac{\text{wt of Ni on powder x Area of control specimen}}{\text{wt of Ni on control specimen}}$

For spherical surfaces



Volume of Ni of thickness "t" plated on sphere of radius "R"

$$= 4/3\ \Pi(R+t)^3 - 4/3\Pi R^3$$

$$= 4/3\ \Pi[(R+t)^3 - R^3]$$

$$= 4/3\ \Pi(3Rt^2+3R^2t+t^3)$$

Also, Volume of Ni $= \frac{\text{Weight of Ni plated on sphere } (\omega)}{\text{Density of Ni } (\rho)}$ or $\frac{\omega}{\rho}$

That is $4/3\ \Pi(3Rt^2+3R^2t+t^3) = \frac{\omega}{\rho}$

Now Area of Ni film $= \frac{\text{Volume of Ni film}}{\text{Thickness of Ni film } (t)}$

$$= \frac{4/3\ \Pi(3Rt^2+3R^2t+t^3)}{t}$$

$$= 4/3\ \Pi(3Rt+3R^2+t^2)$$

Also Area of Ni film $= \frac{\omega}{\rho t}$

Therefore $\frac{\omega}{\rho t} = 4/3\ \Pi(3Rt+3R^2+t^2)$

For $\frac{\omega}{\rho t}$ to give the area of the sphere of radius "R", $4/3\ (3Rt+3R^2+t^2)$ must equal $4\Pi R^2$, area of a sphere.

This will be possible only for values of "t" that are small compared to the values of "R" so the terms 3Rt and t^2 can be ignored.

When "t" is too large, values for the area of the powder determined by:

$$A = \frac{\omega}{\rho t}$$

and Area of powder $= \frac{\text{wt of Ni on powder x Area of control specimen}}{\text{wt of Ni on control specimen}}$

will be low

Although powder particles will not be perfect spheres most will have curved surfaces and the above condition should apply.